Exponent®

Characterization of Ambient Conditions in the Chicago River Upstream from the North Branch MGP Sites

Exponent®

Characterization of Ambient Conditions in the Chicago River Upstream from the North Branch MGP Sites

Prepared for

The Peoples Gas Light and Coke Company
130 East Randolph Drive
Chicago, Illinois 60601

Prepared by

Exponent
1800 Diagonal Road, Suite 300
Alexandria, VA 22314

Revision 1

August 2009

Doc. no. MY03195.006 0104 1108 MK24

Contents

List of Figures

List of Tables

1 Background and Objectives

The term "ambient sediments" is used within the context of a site assessment to indicate those sediments present in the river system that are not influenced by conditions related to the specific site under investigation. By convention, these sediments are usually identified as the sediments located upstream or otherwise out of the potential influence of a site or sites. Characterizing ambient sediments is important because it provides the basis for identifying conditions that are influenced by the site. This document presents the approach to characterize ambient sediment conditions upstream from the former manufactured gas plants (MGPs) at the Division Street, Hawthorne Avenue, Willow Street, and North Station sites (the North Branch MGP sites). This approach will also be applied, as appropriate, to the North Shore Avenue Station MGP site (located upstream of these North Branch MGP sites) as well as the South Branch MGP sites (22nd Street, Throop Street, South, Hough Place, and Pitney Court Stations) and the Crawford Station Site at a later stage. Figure 1 presents the MGP site locations. The North Shore Avenue Site is located many miles upstream of the North Branch MGP sites and thus is not expected to impact the Chicago River near the North Branch MGP sites. MGP sites usually only have a localized affect on sediment quality within a riverine environment. Therefore, ambient characterization at each spatially distinct site (North Shore Avenue Station MGP site) or group of sites (North Branch MGP sites and South Branch MGP sites), will be performed separately.

The concentrations and composition of polycyclic aromatic hydrocarbons (PAHs) are considered the most important aspect of defining ambient, as these compounds tend to be the ones that contribute to the risks associated with sediments adjacent to former MGPs. Metals and select other compounds will also be characterized.

The importance of considering ambient sediment conditions was highlighted in the multi-site risk assessment framework (RAF) document used as the risk assessment guide at these MGP sites (Exponent 2007). Because the Chicago River has a long history of urban and industrial development, the sediments are expected to reflect historical inputs, and there is the probability that some ambient sediments will be toxic to benthic invertebrates based on these inputs. For these reasons, the approach used to define ambient conditions must consider these possibilities

and be sufficiently robust to identify departures from ambient conditions that are site-related. Thus, characterizing the ambient sediment quality upstream from the former MGP sites will provide the necessary data to determine the extent of MGP-related contamination to the river and the increased risk caused by this contamination, if any. The objectives for the ambient sediment characterization include:

- Characterize the ambient chemical composition to distinguish MGP impacts from ambient impacts
- Characterize whether the ambient sediments have the potential to support benthic invertebrates.

The objective for chemical characterization of ambient conditions of the Chicago River was to be able to provide a distinction between MGP-related chemical concentrations and ambient concentrations. A stratified random sediment sampling design was used to select sampling stations within an "ambient zone" of the Chicago River upstream of the North Branch MGP sites. Twenty surface sediment samples will be collected to assess ambient conditions within the river. These 20 ambient surface sediment samples will be collected in areas located upstream from the North Branch MGP sites and also away from other potential industrial sources (i.e., either historical or current) of PAH contamination to the River. In addition to samples that will be used to characterize ambient conditions, five or more additional sediment samples will be collected near potential upstream sources of PAHs. These sources would include major stormwater outfalls and locations immediately adjacent to industrial sites known to make use of coal-tar or petroleum-based products. The samples from these potential source areas will be archived (stored frozen at −20°C) and analyzed for PAHs and metals as necessary to help resolve confounding factors that may arise in the assessment of ambient conditions. The frozen samples will not be used for toxicity testing. Based on an EPA report titled, *Sample Holding Time Reevaluation*, dated November 2005 freezing at −20°C will preserve the PAHs in sediment samples (U.S. EPA. 2005).

The characterization of ambient conditions will focus on surface sediments, operationally defined as the upper 6 in. However, there may be a need to understand historical ambient

conditions. For this reason, a subset of five of the ambient sample locations will also be vertically profiled to assess the chemical distribution in the sediment with depth. These deeper samples will be archived (stored frozen) in the event such information is needed in the future.

As noted, ambient surface samples will be analyzed while source area samples and samples collected at depth will be archived (frozen) and analyzed for PAHs and metals only if MGP site-specific conditions require further evaluation to explain differences between ambient conditions and samples collected in the immediate vicinity of a MGP site. Chemical characterization of ambient sediment samples will include analysis for constituents related to former MGP activities, including PAHs, petroleum volatile organic compounds (PVOCs), phenols, metals, and cyanide. The list of chemical constituents is provided in Table 1 of the RAF. In addition to the chemical constituents, sediments will be analyzed for grain size and total organic carbon (TOC). Chemical concentrations in ambient sediment samples will be used to characterize the mean, range, and upper limit (e.g., upper tolerance limit [UTL]) of concentrations representative of ambient conditions unrelated to former MGP activities. The chemical analyses will also include chemical fingerprinting to help differentiate between PAHs in ambient areas and those associated with the North Branch MGP sites.

Because of the history of industrial and urban activity along the Chicago River, the ambient sediments could exhibit some toxicity to benthic invertebrates, and because toxicity measurements and predictions are used to evaluate the risks associated with exposure to sediments influenced by MGPs, the presence of toxicity in the ambient locations could be a confounding factor. Therefore, it is important to evaluate the level of toxicity that may be present in the ambient samples. This information can be used in various ways, as described in the work plan. However, one of the following outcomes and associated assessment decisions is anticipated:

1. The ambient sediments do not exhibit significant toxicity compared to the control samples used in the laboratory. This outcome indicates that toxicity tests will be useful for determining whether the North Branch MGP sites are contributing to toxicity, and that sediment samples collected off MGP sites

can be evaluated by comparing them with both the ambient samples and laboratory controls.

2. The ambient sediments exhibit some toxicity and many of the samples may be significantly different from the laboratory control samples. This outcome indicates that there is some level of toxicity associated with ambient conditions and that level of toxicity needs to be factored into the evaluation of toxicity for sediments at the MGP site. The information can also be used to determine the test sample size needed to detect a specified degree of increasing toxicity (e.g., 20 percent) for sediments potentially influenced by the MGP.

3. The ambient sediments exhibit substantial toxicity and it would be difficult to detect incremental increases in toxicity. This outcome suggests that toxicity testing at downstream sites may not be able to detect an added influence associated with the MGP. With this outcome, the need to conduct toxicity testing should be re-evaluated, because the testing may provide little value.

It is anticipated that Outcome 2 is most likely followed by Outcome 1. Outcome 3 is a possibility.

2 Ambient and Source Specific Sampling

2.1 Selection of the Chicago River Segment for Ambient Sampling

Ambient sediment conditions will be defined within a 1.3-mile segment (approximately) of the Chicago River upstream from the North Branch MGP sites (Figure 2). This segment is not affected by the former MGP sites, but has been influenced by the general urban Chicago environment and would best represent the ambient conditions near the sites.

2.2 Selection of Potential Sample Locations within the Ambient Segment

In order to have a randomized basis for selecting the 20 ambient samples, the ambient zone was partitioned into twenty-one 100-m long reaches with four polygons per reach (i.e., 84 polygons). Within each 100-m reach, there were 4polygons equivalent to approximately one-quarter of the river width and 100 m long were located (Figure 2); thus, ambient samples will potentially be collected over a 2,100-m segment of the river. The four sample polygons within each 100-m reach include two near shore samples and two main channel samples. A total of 10 near shore and 10 main channel samples will be collected. The two zones (near shore and main channel) will be compared to one another to evaluate if there is any difference in ambient concentrations between these two zones. A potential sediment sample location was randomly placed within each polygon so that sampling would not be biased within the polygon if it were used to characterize ambient conditions. It is recognized that within each reach there may be influences from specific urban areas sources (e.g., major stormwater outfalls, facilities using coal-tar or petroleum-based materials). These polygons, influenced by obvious and known apparent PAH sources, *will not* be selected for the ambient sampling, but rather will be considered for collecting samples for possible future characterization of sources.

In addition to the 20 ambient samples, a minimum of 5 source area surface sediment samples will be collected at locations where PAH sources are suspected. These samples will be archived (frozen). These source samples will not be randomly located within the polygon, but will be located close to apparent PAH sources to maximize the chemical "signal" associated with the source. The purpose of these source samples is to define the chemical fingerprints of PAHs sources affecting this stretch of the Chicago River as well as the relationship between these sources and overall ambient conditions. Potential source areas based on historical information (e.g., review of Sanborn fire insurance maps) or based on current knowledge of land use are shown on Figure 3. There has been diverse historical commercial/industrial use of the properties adjacent to the Chicago River either within the proposed ambient zone or between the ambient zone and the Division Street Station site (Figure 3). The land uses include:

- Metal forging and fabrication
- Bulk storage of petroleum products
- Chemical manufacturing of soaps, paints and varnishes, and pesticides
- Tanneries
- Scrap yards
- Coal storage
- Ship yards
- Asphalt pavement manufacturing.

Of the historical commercial/industrial uses listed above, asphalt pavement manufacturing and bulk storage of petroleum products are the land uses that have the greatest potential to have contributed PAHs to the river. For this reason, when sampling in the ambient zone these areas will be treated as potential source areas. It is assumed that storm sewer outfalls were discharge points where contaminants from these sources and general urban street runoff may have entered the river. Therefore, source area surface sediment samples will be collected where storm sewer outfalls are located that correspond to a potential PAH source to characterize potential

contamination. Outfalls will be mapped as an initial field effort because the number and location with respect to potential source areas is not known. Once the outfalls are mapped and reviewed in relation to the potential source areas shown on Figure 3, a minimum of five specific source area sample locations will be selected. Based on the spatial distribution of the outfalls and the location of selected source area samples, the ambient sample locations will be determined to provide for good spatial representation of the ambient zone. The number of ambient samples collected from a 100-m reach (i.e., 2 samples or all 4 samples) will be determined after the source area samples are identified in the field. Two possible sampling schemes will be considered. Examples of each sampling scheme are included in Table 1.

Sampling Scheme 1—Sampling all four potential ambient sediment samples from a given 100-m reach (i.e., left bank, left main channel, right main channel, and right bank samples).

Sampling Scheme 2—Alternatively sampling every other ambient sediment sample within a reach (i.e., left bank and right main channel samples collected from a reach followed by the right bank and left channel sample from the next upstream reach).

In both schemes, the samples would be numbered consistently across the channel (1, 2, 3, 4). In the latter sampling scheme, samples 1 (left bank) and 3 (right channel) would be sampled in a reach and then in the next upstream reach sample 2 (left channel) and 4 right bank) would be collected. This would allow for a bank and main channel sample to be collected within each reach, and would provide an equal representation of the left and right banks and main channel as the sampling progresses upstream.

If many source areas of PAHs are identified during the initial mapping of source areas, then sampling scheme 1 would be more advantageous in providing the spatial scale that is desired. The intent of the ambient sampling design is to avoid source areas within the ambient area when collecting the ambient sediment samples. Sampling scheme 1 is the preferred scheme and sampling scheme 2 would be used only if source areas within the ambient area are too numerous to make sampling scheme 1 feasible. Note that a limited number of source area sediment samples will collected in the ambient area and archived for possible forensic analyses, but the primary goal of the ambient characterization is not to sample source areas. The source areas

samples in the ambient area will only be used if it is necessary to distinguish between source area contaminations from MGP sources in the investigative area from contamination originating from sources areas in the ambient area.

Sample locations will be refined after an initial field reconnaissance. Once the sample locations are initially selected based on the reconnaissance, the proposed sample locations will be provided to the U.S. Environmental Protection Agency (EPA) for review and comment. The final selection of sample locations incorporating EPA feedback will be provided to EPA prior to collecting the sediment samples.

3 Chemical Characterization of Ambient Conditions

This section describes the strategy that will be used to characterize ambient chemical conditions upstream of the North Branch MGP sites. Chemical characterization will focus on the origin and distribution of individual PAHs in sediments, as this will be the strongest line of evidence to distinguish MGP-related impacts from the impacts of PAHs resulting from other sources. Other chemicals of potential concern (CoPCs) associated with North Branch MGP sites (Table 1 of the RAF) will also be considered because of the historical industrial land use along the Chicago River.

3.1 Number of Ambient and Source-Specific Samples

A minimum of twenty-five sediment samples will be collected to evaluate ambient and source conditions at the site, they will be distributed as follows:

- Twenty sediment samples will be collected within reaches *not* located near identified PAH sources
- A minimum of five sediment samples will be collected within reaches *potentially influenced* by historical or current PAH sources (e.g., outfalls). The objective is to collect samples from a minimum of five reaches containing stormwater outfalls where source areas were historically present.

A surface sediment sample consisting of the top 6 in. (0−0.5 ft) will be collected at each location (i.e., ambient or source area). The 20 ambient surface sediment samples will be distributed evenly among the polygons within the reaches that are identified to be outside of source areas. As described previously, depending on the spatial distribution of the potential ambient samples, the number of samples collected from a 100-m reach (i.e., 2 sample or all 4 samples) will be determined after the source areas are identified in the field.

In addition to the surface samples, at every fourth ambient surface sample station, a core will be collected to vertically define the chemical characteristics of the sediments (total of five cores). Each sediment core will be subdivided into discrete 1-ft depth intervals that mirror the sampling strategy used for the site-specific MGP site sediment investigations. The end depth of the vertical profile will be limited to the thickness of the soft-sediment layer at the sample location. Sediment sampling will start north of the Willow/Hawthorne stations and proceed upstream until all 20 ambient and 5 source area sediment samples are collected.

All of the ambient surface sediment samples (i.e., 20 total) will be analyzed for an expanded list of PAHs (including alkylated PAHs), PVOCs, phenols, metals, and cyanide. In addition to these chemical constituents, the sediments will be analyzed for grain size and TOC. The source area sediment samples and subsurface sediment samples will be archived (frozen) and analyzed for PAHs and metals only if necessary based on site-specific chemical results.

The 20 samples were selected to provide a statistically accurate estimate of the mean and UTL of ambient chemical concentrations. In addition, this number of samples provides a reasonable database for meaningful comparisons of the PAH fingerprinting results. Additional ambient sampling will be considered to supplement what has been proposed herein if it is determined that the data set is not robust enough to meet the project data quality objectives based on the variability of the sediment analytical results. However, until the initial data are collected and evaluated, the need for additional sampling remains unclear.

3.2 Analytical Requirements

Surface sediment samples will be analyzed for an expanded list of PAHs (including alkylated PAHs) using EPA's Method 8270 (gas chromatography/mass spectrometry), a standard practice for PAH chemical fingerprinting. The samples will also be analyzed for PVOCs, metals, and cyanide as listed in Table 1 of the RAF. In addition to the chemical constituents, the sediments will be analyzed for grain size and TOC. These analyses will be performed according to the methods listed in the site-specific quality assurance project plan for the site. These analytical data will be used to define the ambient conditions of the Chicago River upstream from the

former MGP sites and for comparison with PAH, PVOC, phenol, metal, and cyanide results from the former MGP sites.

Archived source and subsurface sediment samples will be frozen at −20°C and analyzed only for the expanded list of PAHs and metals defined in Table 1 of the RAF. The main purpose for these archived samples is to help evaluate the potential source of the constituents.

3.3 Data Analysis

The data for the ambient samples and the source areas samples will be analyzed separately to provide statistics for each of these groups of samples. EPA's most current version of the ProUCL statistical software package will be used to calculate summary statistics and develop an estimate of the mean and 95th UTL (i.e., 95th percentile with 95 percent coverage). This statistical package is designed to test the underlying distribution of the data (e.g., normal, log-normal, gamma, or other). Where a defined underlying data distribution cannot be defined, the program allows for a number of nonparametric methods to estimate the UTL. The UTL will be used for sample-by-sample comparison of total PAH concentrations (or any other CoPCs) with the investigative data. The investigative sediment samples will be defined as those sediment samples collected adjacent to or downstream of the former Division Street MGP, excluding the upstream transect samples, which will be considered ambient sediment samples. The investigative sample set is estimated to include up to 40 sediment sampling locations adjacent to or downstream of the former Division Street MGP. Samples collected in the investigative areas below the UTL will be considered to be within ambient conditions.

The "sample-by-sample" comparisons described above will be between the 95th upper tolerance limit on the 95^{th} percentile (95% UTL) calculated from the ambient sample data set (excluding all source samples) and each investigative sample location concentration. An upper tolerance limit is by definition a one-sided upper limit on the selected percentile (i.e., 95^{th} percentile in this case) similar in nature to the upper confidence limit (UCL) on the mean. The 95 % UTL for total PAHs developed based on the ambient data set will be used to gauge which areas within the investigative area are affected by past MGP activities, and which areas are comparable to ambient conditions.

This approach is used as a screening tool to distinguish site-related impacts from ambient conditions. Other forensic techniques described below will be used as needed to distinguish ambient PAHs from MGP related PAHs.

Comparison of individual sample concentrations with the 95% UTL will liberally identify locations with concentrations above ambient conditions that may be masked by comparing the mean concentrations. However for some analytes (metals for example) where there may not be site-related impacts, the comparison of means (using a one-tailed test) will be performed to control for the overall false positive error rate that may occur using the UTL approach. The 95% UTL comparisons will still be used to identify specific sediment sample locations exceeding ambient conditions for a specific metal when the site mean metal concentration is significantly higher than the ambient mean metal concentration. PAHs attributable to ambient conditions may be differentiated from the MGP PAHs through the application of chemical fingerprinting techniques including:

- **PAH Profile Comparisons—**The characteristic PAH compositional profile of the ambient samples will be compared with the apparent non-MGP sources, and compared with MGP source samples (i.e., tar) to determine the extent of the MGP impacts to the river.

- **Diagnostic PAH Source Ratio (the concentration of one PAH compound relative to another)—**These methods have been used for identifying the sources of PAH contaminants in sediments. For example, ratios such as phenanthrene/anthracene (P/A) and fluoranthene/pyrene (FL/PY) have been used to differentiate between pyrogenic PAH sources (Boehm 2006). These ratios are used as input to perform statistical analysis of the data (described below).

- **Statistical Tools Including Principal Component Analysis—**Principal component analysis is the primary statistical tool used to condense a complex set of variables used to fingerprint a sample—the relative PAH compound concentrations in every sediment sample—down to a series of surrogate factors that explain much of the variability in the data set.

4 Biological Characterization of Ambient Conditions

A second object of the ambient sediment sampling is to characterize whether sediment in the Chicago River can support benthic invertebrates (e.g., caddis, mayflies, and true flies). As specified in the multi-site RAF document, sediment toxicity testing may be incorporated on a site-specific basis to evaluate the zones of risk within the aquatic environment based on toxicity to benthic invertebrates. Because these benthic invertebrates live the majority of their life cycle in the surface sediments (generally top 6 in. or less), they are at most risk to MGP-related constituents in the sediment. However, in the case of the Chicago River, it is possible that the ambient river conditions impose enough stress on the benthic invertebrates, that ambient conditions may be toxic to the test organisms. For this reason, as part of the ambient conditions characterization, the toxicity of the surface sediments will be evaluated.

A portion of 10 ambient surface sediment samples will be tested for toxicity using the 21-day *Hyalella azteca* toxicity test specified in the multi-site RAF. The 10 samples will be distributed evenly throughout the portion of the ambient zone that is ultimately sampled. It is envisioned that sediment from every other ambient surface sediment sample station will be submitted for toxicity testing. Thus, a total of five near shore and five main channel samples will be evaluated. This toxicity test includes an evaluation of organism survival and growth. Ten samples are considered sufficient to provide a clear indication of whether the ambient zone sediments are or are not toxic to the organisms. However, depending on the results of these initial 10 samples, it may be determined that further ambient sampling will be required to evaluate the utility of the toxicity testing if the sample results are in a gray zone (i.e., not clearly toxic or nontoxic). Surface sediments will be used for biological testing because this is the layer where conditions are normally suitable for the organism to live (e.g., oxygen concentrations are sufficient). The range of response in the 10 samples will be evaluated to determine whether the toxicity data indicate that there are consistent conditions present in the ambient area that are either supportive of or detrimental to organism growth and survival. This information will be used to evaluate whether toxicity testing will be a helpful to define areas of potential ecological risk at the specific North Branch MGP sites. If, for example, ambient samples show little toxicity to the organisms, then toxicity testing would clearly be a useful line of evidence in the

ecological risk assessment. If on the other hand, the ambient sediments are consistently toxic to the organism, then conducting toxicity testing would not help to define incremental levels of risk associated with MGP-related chemicals. The sediment toxicity data collected for the ambient zone will be taken into account when evaluating the sediment toxicity data for the individual North Branch MGP site investigations.

5 References

Boehm PD. 2006. Polycyclic aromatic hydrocarbons. In: Environmental Forensics—A Contaminant Specific Approach. Elsevier.

Exponent. 2007. Multi-site risk assessment framework, former manufactured gas plant sites, Revision 0, September 2007.

U.S. EPA. 2005. Sample Holding Time Reevaluation. U.S. Environmental Protection Agency, National Exposure Research Laboratory. EPA/600/R-05/124